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FINAL REPORT - NEGATIVE ION STABILITY CALCULATIONS

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for

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1. General

Calculations have been performed as specified in the contract to determine the energies of $N^- (^1D)$ relative to $N (^2D)$, of $N^- (^3P)$ relative to $N (^4S)$, of $O^- (^2P)$ relative to $O (^3P)$, and, in addition, of $F^- (^1S)$ relative to $F (^2P)$ and of $C^- (^4S)$ relative to $C (^3P)$. These calculations clearly indicate that $N^- (^1D)$ is metastable, lying below $N (^2D)$, that $N^- (^3P)$ is unstable relative to $N (^4S)$, and that the methods of calculation are reliable. This work is described in detail in an appendix to this report entitled "Metastability of the 1D state of the Nitrogen Negative Ion." It is planned to submit this material for publication in Physical Review Letters or in some other appropriate journal.

One copy of certain material produced in the calculations is simultaneously with the submission of this report being transmitted to the Technical Monitor. This material, though not essential to the report, may be of use if Ames Research Center desires to make studies of additional properties of the atoms and ions here investigated. In particular, the material includes previously produced descriptions of the detailed methods of calculation and explicit wavefunctions for certain of the stable and metastable species investigated.

II. Certification

On behalf of the Contractor, it is hereby certified that the level of effort specified in Article I of the contract was used in its performance.

Signed, _____

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APPENDIX

Metastability of the 1D State of the Nitrogen Negative Ion*

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Abstract

Energies of the 3P and 1D states of N^- have been calculated using a first-order wavefunction designed to include the strongly structure-dependent part of the correlation energy. Comparing the N^- calculations to those of other appropriate systems, the remaining correlation energy is reliably estimated and the $^1D N^-$ state is predicted to be metastable, lying 0.844 eV below the 2D state of N. Instability of the $^3P N^-$ state is predicted.

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Several experiments¹ have indicated the existence of one or more states of the ion N^- . However, as the lowest state of atomic nitrogen lies below most estimates of the energy of a hypothetical 3P ground state of N^- , the indicated N^- state(s) may be metastable with respect to electron detachment.² A 3P state of N^- could be expected to decay rapidly into a free electron plus the ground 4S state of N. Bates and Moiseiwitsch³ have suggested that a 1D state of N^- might be stable relative to all excited states of N, and would have a long lifetime because the process



is forbidden. This letter reports calculations comparing the energies of $^1D N^-$ and the first excited state (2D) of atomic nitrogen.

Our calculations are based on wavefunctions designed to include in a nonrelativistic formulation the Hartree-Fock energy plus that part of the correlation energy which depends strongly upon the symmetry and shell structure of the electronic configuration. Such wavefunctions will then be subject to errors resulting from the omission of the remainder of the correlation energy and from relativistic effects. These residual errors, which vary smoothly with respect to the nuclear charge and number of electrons in an atomic system, can be closely estimated by interpolative methods.⁴ This type of partitioning of the corre-

lation energy was suggested by Silverstone and Sinanoğlu⁵, and we call the structure-sensitive part of the correlation energy the orbital correlation energy.

To calculate the orbital correlation energy we use what we call the first-order wavefunction, defined to be a configuration interaction L-S eigenfunction including all orbital occupancies in which at most one electron is assigned to an orbital beyond the valence shell. For first-row atoms, this means configurations in which all, or all but one, of the electrons are assigned to Hartree-Fock 1s, 2s, or 2p orbitals. The orbital correlation energy is the difference between the energy of the first-order wavefunction and the Hartree-Fock energy.

Our first-order wavefunction includes configurations of the types suggested for the same purpose by Silverstone and Sinanoğlu, with the difference that their configurations refer to Slater determinants while ours refer to L-S eigenfunctions. Our first-order wavefunction includes determinants which are not included in the Silverstone-Sinanoğlu enumeration, but whose existence depends upon the electronic shell structure. The significance of this difference is indicated by recent work of Sinanoğlu and Öksüz⁶, who find a structure dependent correlation energy of -1.31 eV for 2D_N , while our first-order wavefunction yields an orbital correlation energy of -1.61 eV.

Using first-order wavefunctions with basis sets sufficiently large to give convergence in energy to within 0.0001 hartree, we have calculated the energies of the lowest 2D state of N and the lowest 1D state of N^- . To aid in estimation of the residual errors, we also carried out corresponding calculations on O^+ (2D) and O (1D), and on the ground states of C, C^- , N^+ , N, N^- , O^+ , O, O^- , F^+ , F, F^- , and Ne^+ . Some of these calculations are described in Table I.

The calculated energies were processed by taking differences corresponding to electron affinities of the neutral atoms and positive ions. Following this, the computed electron affinities of positive ions were compared with the experimental ionization potentials.⁷ It was found that the residual error in the electron affinities indeed varied regularly, depending mainly on the number of electrons, and that a rather good estimate of the electron affinity of a neutral atom could be obtained by assuming the calculated value to have the ^{same} residual error as was found for the electron affinity of the isoelectronic positive ion. Affinities estimated on the basis of this simple assumption are shown in Table II.

Better estimates of the electron affinities of neutral atoms can be produced by noting that the results just cited deviate from experimental values by amounts approximately proportional to the number of 2p electrons in the neutral atom. There is some theoretical justification for such behavior, as more extensive

ab initio calculations⁸ on B and B⁻ have shown that higher order correlations within the 1s²2s² core contribute relatively little to the electron affinity of boron. Assuming, then, an additional residual error of 0.065 eV per 2p electron, we obtain the final estimates listed in Table II.

For all three atoms whose electron affinities are known, these final estimates agree with the experimental data to within the claimed accuracy of measurement, and we are led to conclude that the estimates for the unmeasured affinities of N (⁴S) and N (²D) are of comparable reliability. We therefore predict the instability of the hypothetical ³P state of N⁻, and the existence of a metastable ¹D state of N⁻ lying 1.539 eV above the ⁴S ground state of N, and 0.844 eV below the ²D N excited state.

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Table I. Energies in hartrees of first-order wavefunctions. These calculations are believed to be within 0.0001 hartree of the exact first-order energy.

State and Atom	No. Configurations	Energy	Orbital Correlation Energy
2D N	195	-54.35547	-0.05932
1D N ⁻	105	-54.30922	-0.04235
2D O ⁺	195	-74.29811	-0.06481
1D O	105	-74.77831	-0.04910

Table II. Estimated and measured values of the electron affinities of neutral atoms, in eV.

	Estimated from isoelectronic positive ion	Final estimate	Experiment
$^3\text{P C}$	1.112	1.242	1.25 ± 0.03^a
$^4\text{S N}$	-0.408	-0.213	--
$^2\text{D N}$	0.649	0.844	--
$^3\text{P O}$	1.201	1.461	1.465 ± 0.005^b
$^2\text{P F}$	3.128	3.453	3.448 ± 0.005^c

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